stops, but when the solution is diluted the reaction can proceed to completion.

3. Sulfur reduces anhydrous selenic acid at 63°. In aqueous solution the reaction takes place at higher temperatures, thus a 94.2% solution of the acid is attacked at 68°, and a 40% solution at 190°.

4. Selenium reduces selenic acid of all concentrations at room temperature, or more rapidly at more elevated temperature. More concentrated solutions are more readily attacked.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF WISCONSIN.]

ON THE REDUCTION OF TELLURIC ACID.[1]

BY E. B. BENGER.

Received August 18, 1917.

The study of selenic acid, presented in the preceding paper, has brought new light on the oxidizing power of that compound. Selenic acid is much more easily reduced than was known hitherto. It seemed of interest to determine whether telluric acid would be reduced by substances which reduce selenic acid.

Tellurium lies in the same group and family as selenium, having the highest atomic weight of the members of the sulfur family.

Sulfuric acid is capable of exerting oxidizing power only when in concentrated solution and at elevated temperatures. Selenic acid, as has been shown, is an oxidizing agent toward hydrogen sulfide and sulfur dioxide at all temperatures and even in dilute solutions. Telluric acid, being analogous to sulfuric and selenic acids, and of higher molecular weight, might be expected to show still greater development of the oxidizing power. However, telluric acid differs, in some important respects, from these similar compounds. It is a solid, whereas both of the others are liquids at the ordinary temperature, it has no such strong affinity for water as that shown by either sulfuric or selenic acids, and it is a much weaker acid, being about as strong as hydrogen sulfide or hydrocyanic acid.[2] In these respects it is quite distinct from the lower members of the group. Tellurium itself, in its atomic weight, is an important exception to the rules underlying the periodic system.

Materials Used.

Telluric Acid.—The telluric acid used was prepared by the method of Staudenmaier.[3] This method, which has been employed in this labora-

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[1] Abstract of a part of a thesis submitted to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

[2] Gutbier, "Studien über das Tellur," Leipzig, 1912.

[3] *Z. anorg. allgem. Chem.*, 10, 189 (1895).

tory frequently, and which gives an excellent product, was carried out as follows:

Tellurium was dissolved in aqua regia and the solution was freed from nitric acid by evaporation with excess of hydrochloric acid. The hydrochloric acid solution was diluted and filtered, and the tellurium precipitated by acid sodium sulfite. After thoroughly washing the precipitated tellurium it was oxidized by nitric acid, the solution evaporated, and the resulting basic nitrate purified by crystallization. The pure crystals were boiled for some time with chromic and dilute nitric acid, the tellurium being thus oxidized to telluric acid. On evaporation the telluric acid crystallized out; it was removed from the mother liquor and recrystallized ten to twenty times to free it from chromium nitrate. All the telluric acid used was made by Dr. E. B. Hutchins.[1]

Tellurium.—Commercial tellurium was dissolved in nitric acid, the solution was evaporated and the resulting dioxide ignited. Hydrochloric acid was used to dissolve the tellurium dioxide, the solution was diluted and the tellurium precipitated with sulfur dioxide, after which it was washed and dried. Potassium telluride was formed by fusing the precipitated tellurium with potassium cyanide, it was dissolved in water and a current of air used to reprecipitate the tellurium. The product made in this way is very pure. Thanks are due to Mr. A. M. Hageman who carried out this process of purification.

Hydrogen Sulfide, Sulfur Dioxide, Selenium and Water.—These substances were prepared or purified as described in the preceding paper.

Reduction by Hydrogen Sulfide.—The action of hydrogen sulfide on telluric acid has been given considerable study because of the question as to the existence of sulfides of tellurium. Oppenheim,[2] Becker,[3] Staudemaier,[4] Brauner,[5] Gutbier and Flury[6] and Gutbier[7] have employed hydrogen sulfide as a possible means of producing tellurium trisulfide from telluric acid or alkali tellurates.

Brauner's research was largely a comparison of the action of hydrogen sulfide upon arsenic, antimonic and telluric acids. The method employed by him consisted of adding an aqueous solution of hydrogen sulfide to a solution of telluric acid in a flask. The flask was closely stoppered and allowed to stand at room temperature. Under these conditions Brauner found that "the first trace of turbidity appeared after twenty-four hours, the first trace of a precipitate after two or three days,

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[1] Univ. of Wis., *Bull.* 119 (1905).

[2] *J. prakt. Chem.*, 71, 270 (1857).

[3] *Ann.*, 180, 257 (1876).

[4] *Z. anorg. allgem. Chem.*, 10, 189 (1895).

[5] *J. Chem. Soc.*, 67, 527 (1895).

[6] *Z. anorg. allgem. Chem.*, 32, 272 (1902).

[7] "Studien über das Tellur," Leipzig, 1912.

and even after being kept in the dark and cold for more than two months only a very small percentage was precipitated." He further states,[1] "In order to precipitate a solution of telluric acid completely by excess of hydrogen sulfide, the closed vessel containing the mixture must be heated in boiling water for six to eight hours at least, so difficult is it to precipitate telluric acid completely." Brauner seems to believe that the action of hydrogen sulfide is to form sulfoxytelluric acid which is probably unstable, breaking down at once with liberation of tellurium and sulfur in the atomic proportion Te : S_3.

Experimental.

An aqueous solution of telluric acid was placed in a small Erlenmeyer flask which was immersed in a paraffin bath. A reflux condenser was attached to the flask to prevent loss of water by evaporation. Through the inside condenser tube was passed a long glass tube, the lower end of which was brought nearly to the bottom of the flask containing the telluric acid. By means of this tube a steady current of pure hydrogen sulfide was bubbled through the telluric acid solution. This arrangement permitted the solution of telluric acid to be treated with hydrogen sulfide, or other gas, for long periods at a time. The loss of water from the solution was small and was compensated for by occasional addition of water through the condenser tube.

Samples of the solution were withdrawn from time to time and tested as follows: The liquid was filtered free from precipitated tellurium and sulfur, acidified with hydrochloric acid, hydrazine hydrochloride was added and the solution boiled. If the solution had been incompletely reduced by the action of the hydrogen sulfide, tellurium appeared as a bluish gray turbidity which increased, on standing, to a well coagulated precipitate.

Experiment 1.—Hydrogen sulfide gas was bubbled through a 10% solution of telluric acid at 115° for twenty-one hours; at the end of this time the telluric acid was completely reduced.

Experiment 2.—30% telluric acid, when treated with hydrogen sulfide at 115°, required thirty-three hours of treatment to bring about complete decomposition.

Experiment 3.—Under the same conditions a 50% solution was completely reduced only after eighty-eight hours of treatment with hydrogen sulfide.

It is thus apparent that hydrogen sulfide decomposes telluric acid slowly, even at temperatures above the boiling point of water. Selenic acid is reduced by hydrogen sulfide in dilute solutions and when cold. Sulfuric acid, on the other hand, is reduced by this reagent only when in concentrated form. The reactivity, toward hydrogen sulfide, of these acids

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[1] *Loc. cit.*, pp. 543, 544.

is at variance with the principles of the periodic system. The order of reactivity is: selenic acid, telluric acid, sulfuric acid. The real exception is probably selenium. J. Thomsen[1] has also shown that the affinity of selenium for oxygen is less than that of either sulfur or tellurium for oxygen.

Reduction by Sulfur Dioxide.—Brauner[2] describes the following experiment on the reduction of telluric acid: "0.270 g. was dissolved in water and heated with 200 cc. of aqueous sulfurous acid in a closed vessel for five hours; the precipitated tellurium was collected on a Gooch filter, washed, and dried in carbon dioxide at 100°; its weight was 0.0167 g., or only about 0.1 of the total quantity (0.1526 g.) which was contained in the acid taken." This appears to be the only record of an experiment showing the action of sulfurous acid on a solution of pure telluric acid.

Experiment 1.—A 10% solution of telluric acid was placed in a small Erlenmeyer flask, with a reflux condenser attached, and sulfur dioxide was passed through the solution. Samples were withdrawn and tested from time to time. Not until the sulfur dioxide had bubbled through the solution continuously for twelve days was a test obtained which indicated absence of tellurium from the solution.

Experiment 2.—A 50% solution of telluric acid was treated with sulfur dioxide under the same conditions as those described under Expt. 1. After the action had continued for thirty-five days, during which time the flow of gas was only interrupted long enough to take samples, the reduction of the acid was still incomplete. The experiment was then discontinued.

The results of these experiments agree with the results of the experiment by Brauner quoted above. The reduction of telluric acid by sulfur dioxide is very slow. The fact that the 50% solution was not reduced completely in thirty-five days of continuous treatment may find an explanation in the accumulation of sulfuric acid in the solution. The fact that such is the case in the reduction of selenic acid by sulfur dioxide has been brought out in the preceding paper.

Reduction by Tellurium.—A small quantity of pure tellurium was placed in a glass tube, sealed at one end, and a few cc. of a 30% solution of telluric acid were added. The tube was then sealed and heated to 110° for three days, after which the solution was removed and tested. No telluric acid was found in the solution, the tellurium having completely reduced the telluric acid, the product being tellurous acid.

Reduction by Sulfur.—Flowers of sulfur and telluric acid in 30% solution were sealed together in a glass tube and heated to 110° for eighteen hours. Upon opening the tube and testing the solution it was found that

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[1] "Thermochemische Untersuchungen," **II,** 279 (1882).

[2] *Loc. cit.*

considerable telluric acid had been reduced but that the decomposition was not complete. An experiment extending over three days brought about complete reduction of the telluric acid.

Reduction by Selenium.—When selenium and 30% telluric acid are allowed to react at 110° selenious acid and tellurous acid are formed. The reaction is incomplete at the end of eighteen hours, but after two and one-half days there is no telluric acid left in the solution, showing that the reduction is complete.

Conclusion.

Telluric acid in aqueous solution of any concentration is reduced by hydrogen sulfide and sulfur dioxide slowly. Tellurium, sulfur, and selenium also reduce solutions of telluric acid.

The difficulty of reduction is not what would be expected from a knowledge of the gradation of oxidizing properties in the two lower members of the family in which tellurium is placed; in fact one would expect telluric acid to be even more readily reduced than selenic acid. Thomsen's thermochemical data, however, show that the oxygen compounds of selenium should be reduced more easily than those of sulfur or tellurium. This has been found to be true.

The author takes pleasure in acknowledging his obligation to Victor Lenher, who suggested the subjects of this and the preceding paper, and under whose inspiring direction the investigations were conducted.

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[CONTRIBUTIONS FROMS THE CHEMICAL LABORATORY OF CLARK UNIVERSITY. I, 1.]

MERCURY VAPOR PUMPS FOR OPERATING AGAINST HIGH PRESSURES.

BY CHARLES A. KRAUS.

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Mercury Vapor Pumps, as originally designed by Gaede,[1] and subsequently modified by Langmuir,[2] have proved invaluable in many instances for laboratory operations. These pumps, however, have been designed primarily with a view to speed of operation and as such have usually required the use of a supporting pump giving a relatively high vacuum. For many laboratory operations the speed is often of necessity determined by other conditions, such as the dimensions of connecting tubes, etc. It seemed worth while, therefore, to design a pump which should obviate the necessity of a mechanical supporting pump.

A good water-jet pump will give a vacuum ranging from 8 to 25 mm. depending on the temperature. It was, therefore, undertaken to design a pump which could be supported by a water-jet pump. It was not found

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[1] *Ann. Phys.*, [4] **46**, 357 (1915).

[2] *Phys. Rev.*, [2] **8**, 48 (1916); *J. Franklin Inst.*, **182**, 719 (1916).